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*Published in:*  
Chemical Record

*DOI:*  
[10.1002/tcr.20018](https://doi.org/10.1002/tcr.20018)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2004

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

ten Brinke, G., & Ikkala, O. (2004). Smart materials based on self-assembled hydrogen-bonded comb-shaped supramolecules. *Chemical Record*, 4(4), 219 - 230. <https://doi.org/10.1002/tcr.20018>

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# Smart Materials Based on Self-Assembled Hydrogen-Bonded Comb-Shaped Supramolecules

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*Received 8 April 2004; Revised 1 July 2004; Accepted 31 May 2004*

**Abstract:** Block copolymer self-assembly and supramolecular chemistry can be combined most naturally to prepare smart polymer nanomaterials. An attractive route is based on comb-shaped supramolecules, obtained by attaching side chains to (co)polymers by physical (non-covalent) interactions. Hydrogen bonding is a key element of our approach. It combines an ease of synthesis with other important approach-specific elements, such as hierarchical self-assembly, strongly enhanced processability, swelling, and cleaving. Functional properties discussed include anisotropic proton conductivity, switching proton conductivity, electronically conducting nanowires, polarized luminance, dielectric stacks (optical reflectivity), functional membranes, and nano objects. © 2004 The Japan Chemical Journal Forum and Wiley Periodicals, Inc. Chem Rec 4: 219–230; 2004; Published online in Wiley InterScience (www.interscience.wiley.com) DOI 10.1002/tcr.20018

**Key words:** self-assembly; nanostructures; supramolecular chemistry; block copolymers

## Introduction

In recent years nanoscience has been promoted strongly as a route towards smart materials.<sup>1</sup> An attractive way to create nanostructured materials in a bottom-up approach employs the inherent self-assembling tendency of selected molecular systems. A potentially most rewarding approach is based on the combination of block copolymer self-assembly with supramolecular concepts.

In the case of organic materials, block copolymers are a natural choice when aiming for periodicities at the nanometer length scale.<sup>2–9</sup> Chemically different chain molecules usually macrophase separate in the melt state due to unfavorable exchange interactions. For low molar mass species this is in general offset by the free energy  $kT$  of thermal motion. For chain molecules this is frequently not the case since the interaction contribution is, in contrast to the thermal motion,

proportional to the chain length. This property is used advantageously by covalently linking chemically different polymers, thus leading to many architecturally and chemically different block copolymers, ranging from simple diblock copolymers to triblock copolymers, star copolymers, ring copolymers, comb copolymers, etc. Macrophase separation being prohibited, microphase separation results in the spontaneous formation of nanostructured materials, involving one or more characteristic length scales in the order of 1–200 nm.<sup>2–9</sup>

In supramolecular chemistry, molecularly matching complementary interactions and shape recognition are used to prepare receptor–substrate supramolecules, which can further

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self-assemble into larger structures.<sup>10</sup> These specific interactions have to dominate the randomizing thermal motion. When chainlike molecules are involved thermal motion is less important and complexation between complimentary polymers, such as the stereo complex of syndiotactic and isotactic poly(methyl methacrylate), requires only a very small favorable interaction per monomer unit. This changes, however, when dealing with chain moieties carrying a few functional groups only. To illustrate this we consider the formation of a hydrogen-bonded comb-shaped supramolecule via the end group interaction between a chainlike amphiphile, such as pentadecylphenol (PDP), and a suitable homopolymer, such as poly(4-vinylpyridine) (P4VP).<sup>11</sup> In order to effectively act as a comb copolymer, the hydrogen bonding between the phenol group of PDP and the pyridine group of P4VP has to be strong enough to dominate the unfavorable P4VP-alkyl interactions.

The formation of comb-shaped supramolecules along these lines thus introduces repulsive interactions within a

single supramolecule that can no longer be easily erased by macrophase separation. In stead, microphase separation occurs very much like that of melt systems involving covalently linked comb (or graft) copolymers. If a layered structure is formed, one layer will consist of the polymer together with the functional end groups of the amphiphiles and the other layer will contain the tail part of the amphiphiles. Assuming stoichiometric conditions, i.e. one amphiphile per polymer repeat unit, the polymer conformations will be essentially 2-dimensional, confined within a layer whose thickness is largely determined by the polymer "diameter" and the size of the functional end group. The other layer resembles a brush with a brush height proportional to the tail molecular mass. There is a delicate balance between the tail length and the strength of the specific interactions underlying the comb formation. If the tail length is too long, the strong stretching of the tail will cost too much elastic free energy. This can no longer be compensated by the specific interaction and macrophase separation will occur. If



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► *Olli Ikkala (born in 1953) obtained his Ph.D. in 1983 from Helsinki University of Technology for the first experimental observations of vortices in Fermion superfluid <sup>3</sup>Helium. Subsequently he joined the Corporate R&D department of Neste Ltd. After a period in applied electrochemistry, he participated in 1991–1994 in a collaboration with Uniax Corporation (U.S.A.) to develop electrically conducting polymers. In 1994 he joined the Department of Engineering Physics and Mathematics of Helsinki University of Technology to establish the polymer physics research group where he is currently professor of polymer physics and molecular nanostructures (1999–) and head of the Center for New Materials (2002–). He was President of the Finnish Physical Society 2000–2003. His research interests are in functional materials created by self-assembly of polymers and proteins, coatings, and conducting gels. ■*

the tail is too short, on the other hand, the randomizing thermal motion will dominate and no self-organization will occur either. As long as comb-shaped supramolecules are formed using simple hydrogen bonding only, taking P4VP(PDP) as a characteristic example, experiments demonstrate that tail lengths of up to ca. 20 CH<sub>2</sub> units can be tolerated before macrophase separation occurs. From 12 CH<sub>2</sub> units on microphase separation occurs. In this and similar cases the characteristic length scale of the self-assembled structures that are formed are obviously rather small, of the order of 3–6 nm. Now, this example deals with a single hydrogen bond; however, even if use is made of multiple hydrogen bonding, the strong stretching of the side chains accompanying self-assembly will probably prohibit the use of polymer-like side chains. Hence, the presence of comb-shaped supramolecules based on hydrogen bonding will in general give rise to periodic structures with a relatively short length scale.

Another, much larger, length scale may be introduced by letting the comb-shaped supramolecule be one of the blocks of a diblock copolymer. In this case the short length scale self-assembling tendency of the supramolecule is combined with the large length scale self-assembling tendency of the block copolymer and hierarchically structured materials are obtained in a most natural way.

During recent years the use of different variants of comb-shaped supramolecules to prepare functional (responsive) materials has assumed enormous proportions.<sup>12–19</sup> In many instances mesogenic units are used to create side-chain liquid crystalline polymers.<sup>12–17</sup> In the case of non-mesogenic amphiphiles, one important line of research advocated by Antonietti and co-workers,<sup>18–19</sup> involves the introduction of the comb-shaped architecture using ionic interactions. In this paper, however, we will concentrate on comb-shaped architectures obtained via hydrogen bonding of non-mesogenic chain-like amphiphiles such as the PDP discussed above. Since the hydrogen bonding interaction is usually considerably weaker than ionic interactions, the thermal reversibility of the bonding is an important additional asset. Several examples will be discussed in order to demonstrate the huge potential of this approach.<sup>20</sup>

### Homopolymer-Based Comb-Shaped Supramolecules

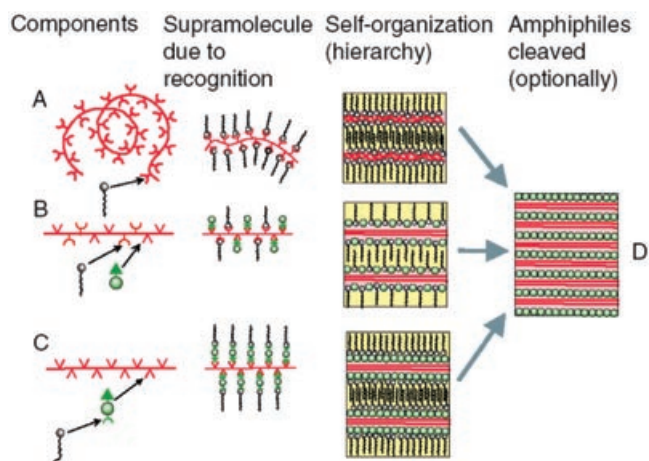
In the case of homopolymer-based supramolecules, the intrinsic flexibility, e.g. flexible versus rigid rod, of the homopolymer is an important additional parameter. A schematic overview of a number of ways that have been used so far to form the hydrogen-bonded comb-shaped architecture is given in Fig. 1.<sup>20</sup> For simplicity, and because this is most frequently encountered in practice, the self-assembly depicted is supposed to lead to a layered structure.

### Flexible Backbone

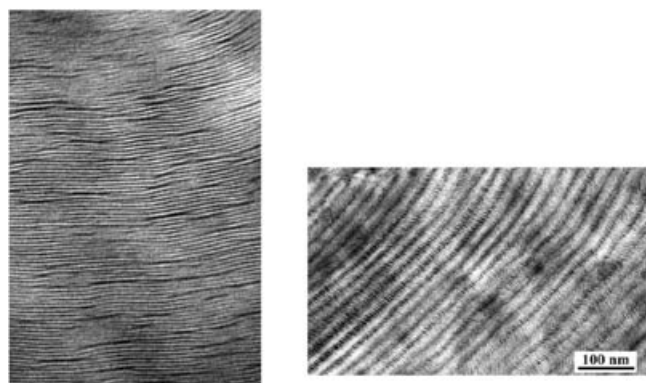
A characteristic example has already been briefly mentioned in the introduction. It concerns the homopolymer poly(4-vinylpyridine) (P4VP) to which pentadecylphenol (PDP) side chains are attached via relatively strong hydrogen bonding between the phenol groups and the pyridine groups. At sufficiently low temperatures, i.e. below ca. 65°C in the case of stoichiometric conditions (one phenol group per pyridine group), the nonpolar alkyl tails are microphase separated from the more polar material.<sup>11,21</sup> Transmission electron microscopy (TEM, Fig. 2) demonstrates that a lamellar structure is formed with a long period of ca. 3.5 nm.<sup>22</sup> As shown by small angle X-ray scattering (SAXS), the microphase separated morphology is formed in the melt below ca. 65°C. At even lower temperatures, the microphase separated system remains fluid until the alkyl tails crystallize around room temperature. Since P4VP itself has a glass transition temperature (T<sub>g</sub>) of 150°C, we observe a huge plasticizing effect. Even though it is in a microphase separated state, the polar layers remain fluid. That the side chain induced self-assembly of P4VP-based systems can actually be used to induce functionality is illustrated by the following example.

### Proton Conductivity

If P4VP is protonated by methane sulfonic acid (MSA), a polysalt is obtained as a simple example of an acid–base complex studied extensively during the last decades in relation to solid state ionics.<sup>23</sup> It exhibits temperature-activated protonic conductivity. PDP still hydrogen bonds to the stoichiometric P4VP(MSA)<sub>1.0</sub> salt and a comb-shaped supramolecule is formed.<sup>24</sup> This particular system undergoes an order–disorder transition to a layered structure at ca. 100°C. Compared with the 65°C for P4VP(PDP)<sub>1.0</sub>, this implies a somewhat larger repulsion in the P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub> system. Here and in the following, the subscripts refer to the number of molecules per repeat unit of the polymer. At elevated temperatures the system goes through an interesting sequence of transitions. At 170°C the PDP first macrophase separates from the P4VP(MSA)<sub>1.0</sub> complex, only to homogeneously mix again at ca. 195°C. Finally, at even higher temperatures, the system macrophase separates again. This closed loop (re-entrant) phase behavior is quite characteristic for hydrogen bonding mixtures.<sup>25</sup> In this case it indicates the presence of a somewhat weaker hydrogen bonding combined with a somewhat stronger repulsion between the two species P4VP(MSA) and PDP as compared to P4VP and PDP. Figure 3 demonstrates this behavior as revealed by optical microscopy. The SAXS data, not reproduced here, confirm the order–disorder transition (ODT) around 100°C. Above the ODT temperature, a correlation hole peak is still present, which on increasing the tem-

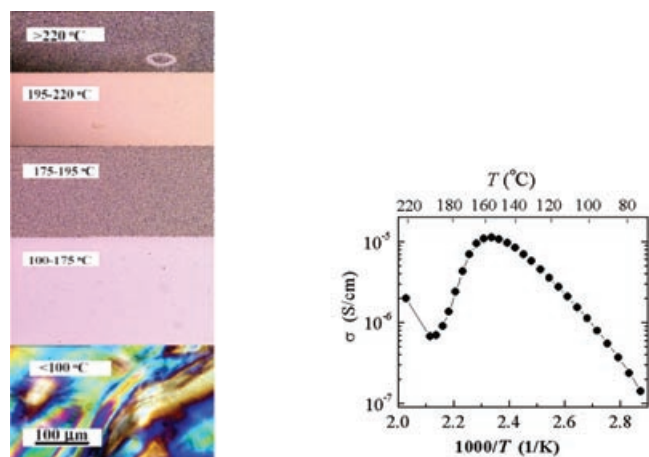


**Fig. 1.** Illustration of formation of comb-shaped supramolecules involving flexible homopolymers (A) or rigid rod polymers (B and C). Different bonding mechanisms and combinations thereof, as well as the option to remove the side chains after the self-assembly has taken place, are indicated. (Adapted from Ikkala and Ten Brinke.<sup>20</sup>)

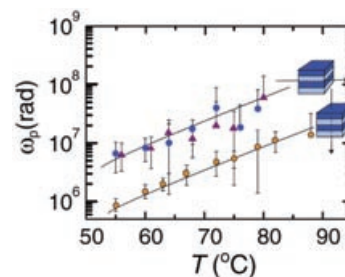


**Fig. 2.** Transmission electron microscopy picture of (left) P4VP(NDP)<sub>1.0</sub> and (right) PS-*block*-P4VP(NDP), where NDP denotes nonadecylphenol. (Adapted from Ruokolainen et al.<sup>22</sup>)

perature decreases in height while shifting to smaller angles. This is a clear signal of a strong decrease in the number of hydrogen bonds.<sup>26</sup> Around 170°C nearly all hydrogen bonds appear to be broken and macrophase separation between PDP and P4VP(MSA)<sub>1.0</sub> sets in. The SAXS data show the corresponding strong scattering in forward direction. Of the sequence of phase transitions in the comb-shaped P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>, only the macrophase separation is directly reflected in the conductivity as a strong drop at 170°C as Fig. 3 illustrates. Because no efforts have been made to align the layers of the microphase separated P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub> the conductivity measured is isotropic, i.e. the same in all directions.



**Fig. 3.** Sequence of optical microscopy pictures of P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub> at indicated temperatures and corresponding proton conductivity. Note the sharp drop around 170°C, due to macrophase separation between P4VP(MSA) and PDP. (Adapted from Ikkala and Ten Brinke.<sup>27</sup>)



**Fig. 4.** Anisotropic proton conductivity in shear aligned P4VP(TSA)(PDP).  $\omega_p$  denotes protonic hopping frequency. (Adapted from Mäki-Onnto et al.<sup>32</sup>)

If instead of MSA toluene sulfonic acid (TSA) is used, the ODT is considerably higher at ca. 140°C, indicating even stronger repulsion.<sup>23</sup> Moreover, at elevated temperatures macrophase separation is not observed. Hence, this stronger repulsion must be accompanied by stronger hydrogen bonding, possibly due to additional phenyl ring stacking. Because of the higher ODT, the TSA-based system is very well suited to explore the possibility of creating materials with anisotropic conducting properties. This can be realised in a relatively simple way by aligning the layered structure by a so-called large amplitude oscillatory shear procedure.<sup>28–31</sup> For the present system this can be achieved at elevated temperatures, i.e. at ca. 130°C and results in a mainly parallel alignment of the layers. As a consequence, an order of magnitude difference in conductivity is observed in the direction parallel to the layers compared to the direction perpendicular to the layers (Fig. 4).



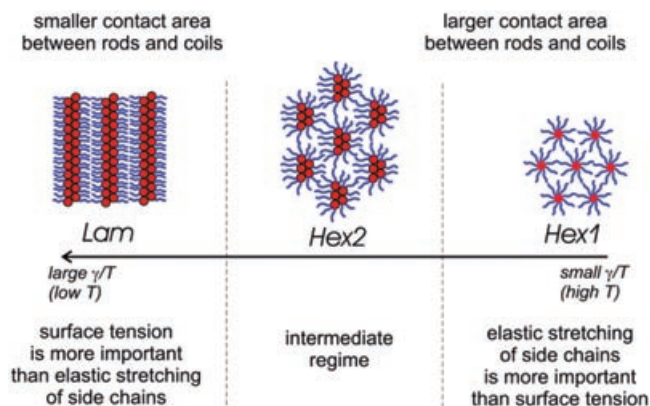


Fig. 5. Predicted formation of microphase separated structures in the case of hairy-rod polymers. If the side chains are relatively short, the "surface tension"  $\gamma$  between the side chains and the stiff backbone is more important than the side chain stretching and a lamellar structure is favoured.<sup>35</sup>

### Stiff Backbone

Many of the most interesting polymers are intrinsically stiff, such as the electronically conducting conjugated polymers. In this case it is in practical terms considerably more difficult to develop functional materials based on the hydrogen bonded comb-shaped supramolecule concept. This is simply due to the fact that rigid polymers are highly incompatible with flexible chain molecules.<sup>33,34</sup> As a consequence, the successful formation of a comb-shape molecule, i.e. a supramolecular hairy rod molecule, usually requires stronger bonding. In the examples to be discussed, this is accomplished using a combination of ionic bonding and multiple hydrogen bonding.

In the limit of a rigid rod backbone, the possible microphase separated states of hairy rod molecules have been theoretically analyzed only very recently.<sup>35</sup> Figure 5 summarizes the different structures possible. From left to right the elastic stretching of the side chains accompanying microphase separation becomes increasingly more important due to an increase in the side chain length and/or side chain grafting density. As long as the stretching of the side chains is relatively unimportant a layered morphology should appear, whereas in the opposite case hexagonally ordered cylinders containing one or more hairy rods are predicted. In the case of hairy-rod supramolecules the possibility of macrophase separation is another complicating factor. In fact, a theoretical analysis<sup>36</sup> shows that such systems will be plagued by macrophase separation unless the composition is carefully chosen. A relative excess of rod molecules will invariably lead to macrophase separation.

### Electronic Conductivity

Polyaniline (PANI) is one of the most interesting polymers in the area of electronically conducting polymers.<sup>37</sup> Protonation

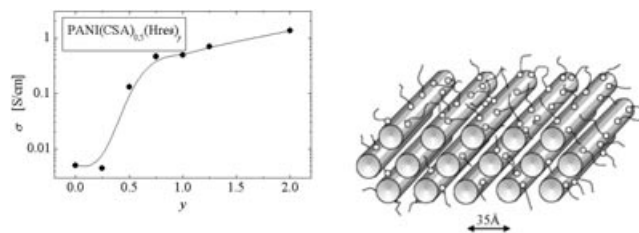


Fig. 6. Electronic conductivity of PANI(CSA)<sub>0.5</sub>(Hres)<sub>y</sub>. Note the sharp increase around  $y = 0.5$  where the hexagonally ordered cylinders appear. (Taken from Kosonen et al.<sup>38</sup>)

of PANI by strong acids is known to render conducting polymer salts. Although rather stiff, PANI is by no means a rigid rod polymer. Therefore, it is to be expected that electrical conductivity of PANI-based systems may greatly benefit from confinement of PANI chains within narrow cylinders. To create cylindrical self-assembled structures hydrogen bonded polyaniline supramolecules were made combining ionic and hydrogen bonding.<sup>38</sup> This combination serves a dual purpose: the protonation introduces the electrical conductivity and the hydrogen bonding allows self-assembly. The iminic nitrogens of PANI were first nominally fully protonated using camphorsulfonic acid (CSA) to yield PANI(CSA)<sub>0.5</sub> and then hydrogen bonded to 4-hexylresorcinol (Hres). Both hydroxyl groups of Hres seem to be required to prevent macrophase separation. As demonstrated by the SAXS data, the resulting rodlike supramolecules indeed self-organize into hexagonally ordered cylindrical structures for a number  $y$  of Hres units per aniline repeat unit in the range of  $y = 0.5$ –2.0. As can be seen from Fig. 6, upon formation of the cylinders that contain 3–4 PANI molecules per cylinder, the electrical conductivity increased two orders of magnitude.

### Polarized Luminance

The following example involves the conjugated polymer poly(2,5-pyridinediyl) (PPY) consisting of para-coupled pyridil rings. It is structurally similar to the PANI system except that now the *cleavability* of the amphiphiles plays an essential role as well: the hydrogen bonded species are removed by a simple evaporation procedure after self-assembly has led to the desired structure. In this way highly ordered solid state films of rigid rod polymers may be obtained. PPY is first protonated with CSA, which in this case leads to an efficient photoluminescence quantum yield.<sup>39</sup> Further hydrogen bonding with octylgallate (OG), allowing multiple hydrogen bonds, leads to comb-shaped supramolecules that can easily be processed and that self-assemble in the form of a layered structure.<sup>40–43</sup> Due to the fluid nature of the thin films, the rod-like entities can be oriented by simple shear. SAXS demonstrates

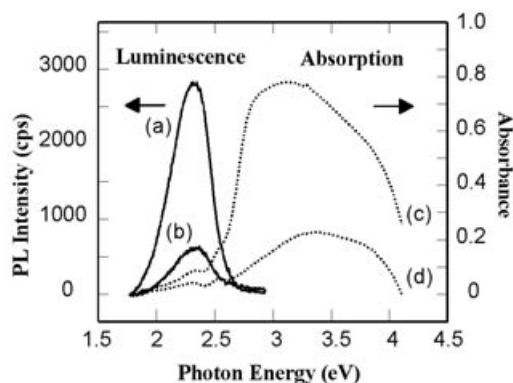


Fig. 7. Polarized luminance of PPY(CSA)<sub>0.5</sub>(OG). (Taken from Knaapila et al.<sup>41</sup>)

that indeed highly ordered structures are formed. After evaporation of OG the corresponding well-ordered solid film is obtained exhibiting polarized luminescence (Fig. 7). Here processability is combined with structure formation and cleavability. In view of the theoretical predictions that supramolecular hairy rod systems are prone to macrophase separation, applications such as these, where the hydrogen bonding species are removed after they served their role in the self-assembly process, seem most promising.

### Block Copolymer-Based Comb-Shaped Supramolecules

If, instead of homopolymers, suitable block copolymers are used as starting materials, characteristic two length scale hierarchical structures may be formed upon complexation with amphiphiles. These systems form the basis for a variety of applications. Characteristic features that are used advantageously include improved processing, doping, swelling, and cleaving. The structure formation and additional cleaving of side chains is schematically illustrated in Fig. 8. The best-studied example involves a diblock copolymer of polystyrene (PS) and poly(4-vinyl pyridine) (P4VP) where pentadecylphenol (PDP) is hydrogen bonded to the P4VP block: PS-*b*-P4VP(PDP). Usually, a microphase separated morphology consisting of PS and P4VP(PDP) domains is present throughout the experimental temperature range (0–250°C) with a characteristic length scale in the order of 10–50 nm. Under stoichiometric conditions, below ca. 65°C the short length scale structure due to the comb-shaped nature of the P4VP(PDP) blocks is formed inside the P4VP(PDP) domains. Lamellar-*within*-lamellar, lamellar-*within*-cylinders and lamellar-*within*-spheres, as well as the complimentary structures have all been demonstrated and imaged by TEM. A characteristic example is presented in Fig. 2.<sup>24,44</sup>

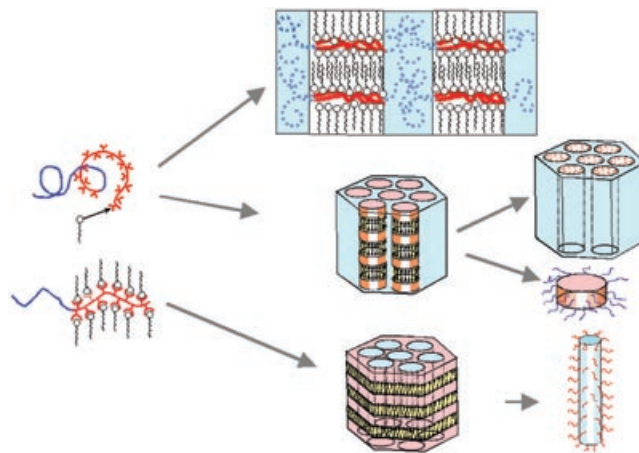
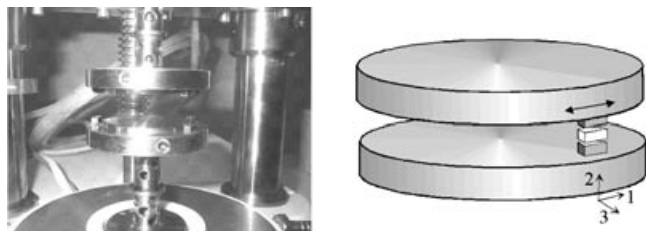


Fig. 8. Illustration of hierarchical structure formation of block copolymer-based supramolecules and subsequent preparation of nano-membranes and nano-objects by removal of the side chains. (Adapted from Ikkala and Ten Brinke.<sup>20</sup>)

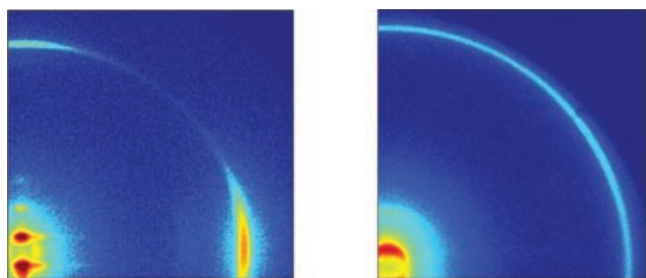
### Tridirectional Protonic Conductivity

An interesting example, where the presence of *hierarchical* structures is explicitly used, involves proton conductivity. As already discussed before, complexation of P4VP with a strong acid, such as toluene sulfonic acid (TSA), creates a proton conducting material. If a stoichiometric complexation with TSA is taken and subsequently combined with the hydrogen bonding PDP amphiphiles, self-assembly leads to a layered structure below ca. 140°C, where the polar layers are proton conducting. If instead of homopolymer P4VP, a suitable P4VP-*b*-PS block copolymer is used, a hierarchically ordered lamellar-*within*-lamellar material, similar to the one illustrated in Fig. 8, is obtained. After applying an appropriate oscillatory shear protocol to such a PS-*b*-P4VP(TSA)(PDP) sample, the macroscopic ordering is improved, although far from perfect.<sup>32</sup>

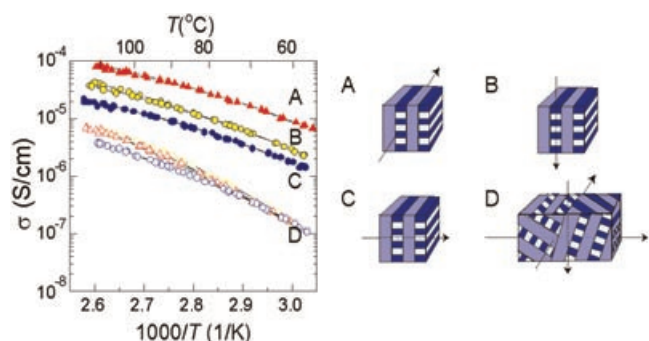
To investigate the effects of large amplitude oscillatory shear on the alignment of lamellar-*within*-lamellar structures, a systematic study was undertaken using as a model system polyisoprene-block-poly(4-vinylpyridine) (PI-*b*-P4VP) diblock copolymer-based PI-*b*-P4VP(PDP)<sub>1.0</sub>. Due to the relatively low glass transition temperature of PI the shear can be applied below the ODT of P4VP(PDP). A specially designed “tooth” rheometer (Fig. 9) was used to measure the radial and tangential two-dimensional small angle X-ray patterns (Fig. 10) of this system taken in-situ during the application of large amplitude oscillatory shear.<sup>45</sup> According to the radial scattering pattern, the structure consists of alternating PI and P4VP(PDP) layers that are aligned parallel to the shear direction. Inside the P4VP(PDP) layers the short length scale ordering is preferentially transverse (cf. Fig. 11 for definition of transverse). The “wide” angle meridional scattering peak in the radial



**Fig. 9.** Illustration of shear procedure using the newly designed rheometer allowing both in-situ radial and tangential measurements. A very small amount of sample is placed between two opposite teeth of equal dimension (e.g. 3 by 8 mm). The oscillatory shear is in the 1-direction. A radial scattering experiment corresponds to the X-ray beam entering via the 3-direction; tangential corresponds to the 1-direction. (Adapted from Polushkin et al.<sup>45</sup>)



**Fig. 10.** Radial and tangential SAXS picture of a PI-*b*-P4VP(PDP) lamellar-*within*-lamellar structure observed in situ during large amplitude oscillatory shear in a synchrotron X-ray beamline.<sup>45</sup>



**Fig. 11.** Anisotropic proton conductivity of aligned lamellar-*within*-lamellar PS-*b*-P4VP(TSA)(PDP). The preferred alignment of the hierarchically structured material corresponds to the arrow in A pointing in the radial ( $\approx 3$  in Fig. 9) direction. Note that the actual periodicity of the internal layers ( $\approx 4$  nm) is an order of magnitude smaller than the large diblock length scale ( $\approx 32$  nm). (Adapted from Mäki-Ontto et al.<sup>32</sup>)

pattern and the wide angle scattering ring in the tangential pattern demonstrate the presence of additional isotropic orientations of the short length scale structure as well. It remains a challenge to produce single crystal-like hierarchically ordered materials.

Returning to the PS-*b*-P4VP(TSA)(PDP) system, we found that it behaved under large amplitude oscillatory shear in much the same way as PI-*b*-P4VP(PDP). The proton conducting one-dimensional slabs, containing the P4VP(TSA) salt, have a similar preferred transverse orientation with respect to the shear direction, with concurrent tridirectional proton conductivity (see Fig. 11). The fact that the alignment is far from perfect results in a still relatively small difference in conductivity in the three different directions.

### Switching Proton Conductivity

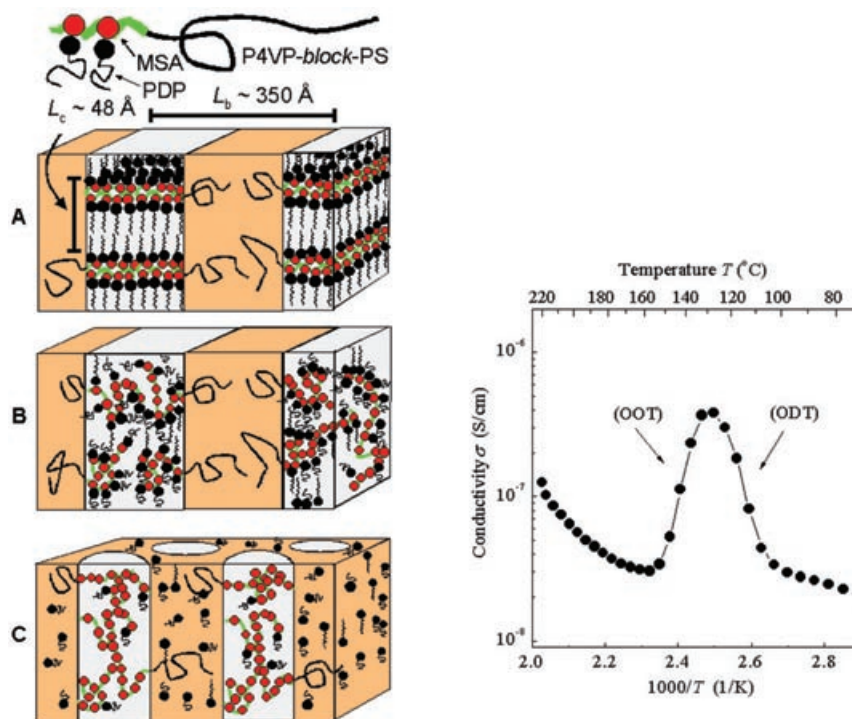
If instead of TSA, MSA is used, the complex phase behaviour observed for the homopolymer-based P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub> gives rise to even more interesting behavior of PS-*b*-P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub>. This is illustrated in Fig. 12, showing a cartoon-like presentation of the different structural transitions and the concurrent temperature switching in proton conductivity. Below ca. 100°C, a lamellar-*within*-lamellar structure is present. Above 100°C, the short length scale lamellar structure disappears at the corresponding order–disorder transition temperature. At higher temperatures the miscibility of PDP with PS improves until they become completely miscible at ca. 135°C. Since, the miscibility of PDP with P4VP(MSA) decreases, PDP gradually diffuses into the PS phase thereby increasing its relative volume fraction. As a consequence, an order–order transition to a hexagonally ordered cylindrical morphology occurs with P4VP(MSA) forming the cylinders.<sup>24</sup>

The SAXS data, not presented here, clearly show the two different lamellar structures below ca. 100°C. At ca. 100°C, the scattering peak that corresponds to the short length scale layers diminishes sharply in intensity, broadens and shifts to smaller angles. This signals the order–disorder transition and a subsequent gradual reduction in number of hydrogen bonds. At ca. 135°C, the large length scale lamellar structure turns into a hexagonally ordered structure as witnessed by a characteristic  $\sqrt{3}$  peak.<sup>24</sup> Concerning the proton conductivity, the main observation concerns the dimensionality of the P4VP(MSA)<sub>1.0</sub> proton conducting domains. As a function of temperature one-dimensionally confined layers turn into two-dimensional layers and then into one-dimensional cylinders. That these transitions are directly reflected in the overall conductivity is demonstrated in Fig. 12. Since self-assembly of block copolymer systems invariably leads to a multi-domain grain boundary structure that is macroscopically isotropic, the conductivity represents an average over all directions with respect to the local oriented structure.

### Photonic Band Gap Materials

Self-assembly in block copolymer systems leads to well-ordered structures which are potentially interesting for photonic





**Fig. 12.** Sequence of structural transitions occurring in PS-*b*-P4VP(MSA)(PDP) as a function of temperature and corresponding proton conductivity of recorded during heating at  $5^{\circ}\text{C}/\text{min}$  based on AC impedance measurements extrapolated to zero frequency. The order–disorder transitions at  $100^{\circ}\text{C}$  and the order–order transition at  $150^{\circ}\text{C}$  are distinctly reflected in the conductivity. (Taken from Ruokolainen et al.<sup>24</sup>)

crystals applications.<sup>46–47</sup> The transport of electromagnetic radiation can be manipulated using photonic band gap materials, which contain periodic structures with sufficiently high dielectric contrast. There are, however, several important problems to be solved before this potential can be fully realized. One of these is the large periodicity required (order of  $\lambda/4$ , where  $\lambda$  is the wavelength of the electromagnetic radiation used). A large periodicity requires high molecular weight block copolymers, which are notoriously difficult to prepare in a single crystal-like state. Here the comb-shaped supramolecules concept may have some advantages as well. Apart from inducing hierarchical structures in the case of block copolymers, the supramolecular side chains especially act as very efficient *swelling agents*. Recently we demonstrated that in the case of high molar mass PS-*b*-P4VP diblock copolymers, the PS-*b*-P4VP(DBSA) supramolecules, where DBSA denotes dodecyl benzene sulfonic acid, form self-assembled one-dimensional optical reflectors.<sup>48</sup> The appearance of PS-*b*-P4VP(DBSA)<sub>1.5</sub>, where the excess DBSA is hydrogen bonded to the PS-*b*-P4VP(DBSA)<sub>1.0</sub> complex, is presented in Fig. 13. The obvious next step consists in exploiting the complex phase behavior of PS-*b*-P4VP(MSA)(PDP), discussed above in connection with



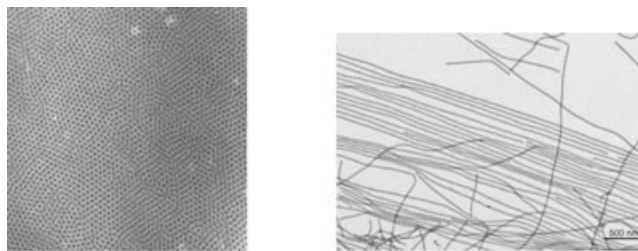
**Fig. 13.** Appearance of PS-block-P4VP(DBSA)<sub>y</sub>, for  $y=1.5$ . (Courtesy S. Valkama and H. Kosonen.)

switching proton conductivity, to prepare materials with reversible switching band gaps.<sup>49</sup> This application demonstrates how the very effective swelling by the side chains leads to the large periodicities required.

### Functional Membranes

From a general point of view, self-assembled periodic structures of block copolymers offer unique possibilities to prepare materials with functional nanostructures such as membranes. Liu and co-workers<sup>50</sup> prepared thin films with densely hexagonally packed nanochannels starting from specific diblock copolymers. Their concept is based on diblock copolymers consisting of a degradable block and a crosslinkable block. Block lengths are selected in such a way that a hexagonally ordered cylindrical structure is formed with cylinders formed by the degradable block. After microtoming the matrix is crosslinked and the cylinders are degraded. They prepared thin films with nanochannels from poly(*tert*-butyl acrylate)-*block*-poly(2-cinnamoyl ethyl methacrylate), where the *tert*-butyl groups are cleavable by hydrolysis and poly(2-cinnamoyl ethyl methacrylate) is photo-crosslinkable. Another concept was recently put forward by Russell and co-workers.<sup>51</sup> The starting point was a hexagonally ordered thin film of diblock copolymers of poly(methyl methacrylate) (PMMA) and polystyrene (PS) (PS-*b*-PMMA) with cylinders containing the PMMA blocks. The cylinders were oriented perpendicular to the plane of the film using a specially modified substrate.<sup>52</sup> By adding homopolymer PMMA of a slightly smaller molecular mass than that of the PMMA-block to the block copolymers, the size of the cylindrical domains could be manipulated without perturbing the spatial order and orientation. Selective removal of the homopolymer produced pore diameters well below that achievable by pure block copolymers, whereas, the removal of both the homopolymer and the corresponding block produced pores that are larger than achievable from the pure diblock copolymer.

This review is primarily devoted to concepts employing materials where amphiphilic molecules are physically bonded selectively to one block of a block-copolymer to form specific comb-shaped supramolecules that self-assemble to form structure-*within*-structures. The cleavability of the supramolecular side chains make these materials ideally suited to prepare nanoporous materials. A very simple example concerns the preparation of membranes containing hollow self-assembled cylinders with polymer brushes at the wall. By proper selection of the PS-*b*-P4VP block molecular weights a cylindrical morphology of the PS-*b*-P4VP(PDP) can be obtained where the supramolecular side chains are inside the cylinders. Thus self-assembly may be used to prepare hexagonally ordered films, where the order extends over macroscopic distances after the application of suitable external fields. The supramolecular side



**Fig. 14.** Left: TEM of a thin film of self-organized PI-*b*-P4VP(OG) comb-shaped supramolecules obtained by hydrogen bonding octylgallate (OG) to a polyisoprene (PI)-*block*-poly(4-vinylpyridine) diblock copolymer. Cylinders are perpendicular to the film surface due to a large amplitude oscillatory shear treatment (Bondzic, S.; Ruokolainen, J. et al., *Macromolecules*, in press). Right: Core-shell rods consisting of a PS-core and a thin P4VP-corona (Taken from Alberda van Ekenstein et al.<sup>54</sup>)

chains, accounting for no less than 75% of the material inside the cylinders, can easily be dissolved afterwards, leaving a porous membrane.<sup>53</sup>

Interesting possibilities arise if instead of the PS-block a low T<sub>g</sub> block such as polybutadiene or polyisoprene is taken (Fig. 14). After crosslinking the matrix (e.g. polyisoprene) and subsequent removal of the complexing additive by simple dissolution, a stretchable nanoporous template is obtained. Using biaxial stretching relatively large nanopores may be obtained to which e.g. appropriate monomers and chemical oxidizing agents can be added. Subsequent partial stress relief results in a porous membrane with cylindrical pores of a controlled diameter, filled with an appropriate solution. In this way for instance conducting polymer fibres confined to nanocylinders of a controlled diameter may be prepared.

### Nano Objects

Self-assembly of block copolymers has been used extensively to prepare individual polymeric “nano-objects”. A general method is based on crew-cut aggregates, where amphiphilic diblock copolymers can be used, such as polystyrene-*block*-polyacrylic acid with a short hydrophilic block.<sup>54,55</sup> Crew-cut aggregates are typically constructed by first dissolving the chains in a solvent that dissolves both blocks and subsequently adding water to cause controlled aggregation of the hydrophobic blocks. It is also possible to use a single solvent in which both blocks are soluble at high temperatures and the aggregation of the hydrophobic block results on decreasing the temperature. A particularly rich variety of polymeric nanostructures is obtainable, including nanoscale rods.

Another method to prepare polymeric nanofibers, nanotubes, and spherical objects is based on block copolymers containing photocrosslinkable moieties.<sup>56,57</sup> In this case, a diblock or triblock copolymer is selected properly to allow the desired morphology in bulk, for example the hexagonal

**Table 1.** Overview of systems discussed.


self-assembly of cylinders if nanofibers are to be prepared. The concept uses the photocrosslinkable block to fixate the structure by photocrosslinking. Ultimately, the fibers and tubes can be “sculptured” based on selective dissolution and/or degradation. Individual fibers of diameter ca. 40 nm were resolved and can even be redissolved in other solvents to allow liquid crystalline solutions.<sup>57</sup> The advantage of this concept is that the design is based on the bulk phases of block copolymers instead of the more complicated solvent phases. However, there is

a limitation that specific photocrosslinkable moieties are required.

The comb-shaped supramolecules discussed at length in this review allow a novel and general concept to prepare crew-cut aggregates<sup>58</sup> as well as more complex shaped disc-like objects.<sup>59</sup> The procedure to prepare crew-cut nano objects is illustrated in Fig. 8 for the case of nano rods. When PS-*b*-P4VP(PDP) supramolecules self-assemble in a hexagonally ordered cylindrical morphology with the comb-shaped

P4VP(PDP) forming the majority phase and PS-cylinders, the dissolution of the side chains will lead to "hairy rods". Figure 14 shows a picture of these nano rods.<sup>59</sup> Other nano objects, potentially even more interesting, may be obtained from lamellar-*within*-cylindrical hierarchical morphologies. Here, crosslinking of the P4VP slices inside the cylinders with 1,4-dibromobutane or 1,4-diiodobutane leaves the microphase separated morphology intact and results in discotic objects of P4VP discs with long PS hairs after dissolution of the side chains (e.g. PDP).<sup>60</sup>

*It has been a pleasure to collaborate on these subjects with many distinguished scientists and skillful graduate students whose names appear in the cited references.*

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